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Task No. 0051-865

Technical Report #33

Silver(II) Tetraneopentoxypthalocyanine and its Redox Chemistry

By

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in

Inorganic Chemistry

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SECURITY CLASSIFICATION OF THIS PAGE

## REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified			3. DISTRIBUTION / AVAILABILITY OF REPORT  As it appears on the report		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)  Report # 33			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada			7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201		
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
11. TITLE (Include Security Classification) Silver(II) Tetraneopentoxypthalocyanine and its Redox Chemistry					
12. PERSONAL AUTHOR(S) G. Fu, Y. Fu, K. Kayaraj and A.B.P. Lever*					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM Aug. '89 to Aug. '90		14. DATE OF REPORT (Year, Month, Day) June 22, 1990	
15. PAGE COUNT 28					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)  Phthalocyanine, Silver, Electrochemistry, Electron Spin Resonance. (JES)		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The synthesis and characterisation of the title complex is described. This new silver(II) phthalocyanine is soluble in most organic solvents rendering it suitable for extended study. The complex can be oxidized electrochemically to a silver(III) phthalocyanine which is also indefinitely stable. Further oxidation is possible to the silver(III) phthalocyanine cation radical also showing substantial stability. Reduction to a silver(I) phthalocyanine leads to demetallation on the electrochemical time scale. In support of this electrochemical study, the electrochemistry of metal free tetraneopentoxypthalocyanine is also reported. Both silver(II) and metal-free tetraneopentoxypthalocyanine are extensively aggregated in solution. The FTIR spectrum of the title complex is compared with the spectra of the corresponding cobalt(II), copper(II) and zinc species. The electronic spectra of the several silver species are reported. When diluted with metal-free tetraneopentoxypthalocyanine, silver(II) tetraneopetoxypthalocyanine yields a highly resolved electron spin resonance spectrum. Spin Hamiltonian parameters are reported.					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Ronald A. De Marco			22b. TELEPHONE (Include Area Code)		22c. OFFICE SYMBOL

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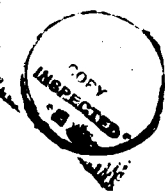
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Silver(II) Tetraneopentoxypthalocyanine and its Redox Chemistry

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**Abstract**

The synthesis and characterisation of the title complex is described. This new silver(II) phthalocyanine is soluble in most organic solvents rendering it suitable for extended study. The complex can be oxidized electrochemically to a silver(III) phthalocyanine which is also indefinitely stable. Further oxidation is possible to the silver(III) phthalocyanine cation radical also showing substantial stability. Reduction to a silver(I) phthalocyanine leads to demetallation on the electrochemical time scale. In support of this electrochemical study, the electrochemistry of metal free tetraneopentoxypthalocyanine is also reported. Both silver(II) and metal-free tetraneopentoxypthalocyanine are extensively aggregated in solution. The FTIR spectrum of the title complex is compared with the spectra of the corresponding cobalt(II), copper(II) and zinc species. The electronic spectra of the several silver species are reported. When diluted with metal-free tetraneopentoxypthalocyanine, silver(II) tetraneopentoxypthalocyanine yields a highly resolved electron spin resonance spectrum. Spin Hamiltonian parameters are reported.

## Introduction

1-6 The +2 and +3 oxidation states of silver can be stabilized by N<sub>2</sub>-heterocyclic and tetraazamacrocyclic ligands and porphyrins,<sup>1-6</sup> but relatively little is known about these higher oxidation state silver species. While silver porphyrins have been studied in some depth, Silver phthalocyanine, although known for a long period<sup>7</sup> has not been seriously studied, probably because of its low solubility in organic solvents.

7 There is currently considerable interest in the development of phthalocyanine species for such high technology applications as electronic sensors, electrochromic displays, computer read-write disks etc.<sup>8,9</sup> Silver phthalocyanine may have significant value in this context.

8,9 Recently, we have obtained the first highly-soluble silver phthalocyanine species, silver(II) tetraneopentoxypthalocyanine (Ag(II)TNPc), and report here the characterisation and properties of this species in several oxidation states. The species forms a Langmuir-Blodgett film whose properties will be described elsewhere.<sup>10</sup>

## Experimental Section

Materials: Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, Aldrich) was recrystallized from absolute ethanol and dried in a vacuum oven at 120 °C for 24 hours. 1,2-Dichlorobenzene (DCB, Aldrich, Gold label) was used as supplied. Dichloroethane (DCE, Aldrich) was distilled over P<sub>2</sub>O<sub>5</sub> before use.

### Tetraneopentoxypthalocyanatosilver(II): (Ag(II)TNPc)

11 Metal free tetraneopentoxypthalocyanine (H<sub>2</sub>TNPc)<sup>11</sup> (0.050g, 5.8x10<sup>-5</sup> Mol). and silver nitrate (0.062g, 3.6 x 10<sup>-4</sup> Mol) were heated in dimethylformamide (10mL) at about 75 °C for about 6-7hrs. Drops of the reaction mixture were removed from time



to time to monitor the electronic absorption at 707nm, due to  $H_2TnPc$ , relative to that at 681nm, due to  $Ag(II)TnPc$ . The reaction was stopped when the 707nm peak had disappeared; the solution was stored overnight at room temperature. The resulting green precipitate was washed with water and acetone and recrystallized from toluene. Yield 0.052g, 93%. (Anal. CHN)

Physical measurements: Electronic spectra were recorded with a Hitachi Perkin-Elmer Model 340 microprocessor Model 340 spectrometer or a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyzer with a WW100 fiber optic probe. Electrochemical data were obtained with a Princeton Applied Research (PARC) model 173 potentiostat, or a PARC model 174A polarographic analyzer coupled to a PARC model 175 universal programmer. Cyclic voltammetry and differential pulse voltammetry (DPV) were carried out under an atmosphere of argon, or nitrogen, using a conventional three electrode cell. The working electrode was described by the cross-sectional area of a 27-gauge platinum wire (area  $10^{-3} \text{ cm}^2$ ), and sealed in glass. A platinum wire also served as the counter electrode. The reference electrode was a small SCE separated from the working compartment by a glass frit, or a silver wire quasi-reference electrode. In the latter case, potentials were referenced internally to the ferricenium/ferrocene ( $Fc^+/Fc$ ) couple.

Controlled potential electrolysis, coulometry and spectroelectrochemical measurements were made by using a bulk electrolysis cell, consisting of a platinum plate working electrode, platinum flag counter electrode, and an SCE reference electrode. Counter and reference electrodes were separated from the working compartment by a glass frit and a salt bridge respectively. Spectra were recorded during bulk electrolysis by immersing the Guided Wave fiber optic probe in the solution, degassed with argon or nitrogen. Solutions for electrochemistry and spectroelectrochemistry contained 0.2-0.4M TBAPF<sub>6</sub>, as supporting electrolyte.

Electron spin resonance data were obtained using a Varian E4 spectrometer cali-

brated with diphenylpicrylhydrazide. Isotropic spectra were measured in a chloroform solution at room temperature. To obtain anisotropic spectra at low temperature, a mixture of toluene and chloroform (1:1,v:v), was used, and a relatively large amount of metal free tetraneopentoxypthalocyanine ( $H_2TNPc$ ) was added to the dilute (about  $10^{-5}M$ )  $Ag(II)TNPc$  solution. A solution of pure  $Ag(II)TNPc$  does not yield a good spectrum at low temperature because of aggregation.

Fourier transform infrared spectra (FTIR) These were recorded as Nujol mulls using a Nicolet 20SX instrument. The principal absorption bands between 600 and  $1800\text{ cm}^{-1}$  are as follows, with data for  $CuTNPc^{12}$   $ZnTNPc^{13}$  and  $CoTNPc^{14}$  for comparison:

$Ag(II)TNPc$	734s	824m	1023w	1057s	1105m	1124s	1238s		1283m	1339m	1609s
$Cu(II)TNPc$	747s	822m	1014m	1061s	1098s	1120m	1239s	1272w	1282w	1344m	1611s
$Co(II)TNPc$	751s	821m	1014m	1065s	1094s	1128s	1239vs	1271w	1283w	1344m	1611s
$Zn(II)TNPc$	744s	823m	1014m	1057s	1094s	1122s	1238vs	1271m	1283m	1339s	1610vs

## Results and Discussion

**Oxidation State:** The ESR spectrum (below) of  $Ag(II)TNPc$  is indicative of the  $d^9$   $Ag(II)$  ion. Further its FTIR spectrum is very similar to those of  $Co(II)TNPc$ ,  $Cu(II)TNPc$  and  $Zn(II)TNPc$  (see expt.). Note however that the FTIR spectra of these last three species are rather more similar to each other, in terms of relative band intensities and band shapes, than they are to  $Ag(II)TNPc$ . Nevertheless there is almost a 1:1 correlation with  $Ag(II)TNPc$  in terms of the number of bands and their positions.

**Solubility and stability in solution:**  $Ag(II)TNPc$  is highly soluble and stable in hydrocarbon and aromatic hydrocarbon solvents, and their chlorinated derivatives and less soluble in nitrogen containing solvents such as dimethylformamide and acetonitrile. It is insoluble in acetone and dimethylsulfoxide. Indeed coordinating

15 solvents such as pyridine, rather than forming axially coordinated solvates as is common with chromium, iron and cobalt phthalocyanines etc., lead to some demetallation as indicated by the electronic absorption spectra of the resulting solutions. AgTnPc is also demetallated by the addition of coordinating ligands such as imidazole, when such nitrogen ligands are added to otherwise stable solutions of AgTnPc, for example, in DCB. This lability of silver phthalocyanine has been attributed to the unfavorable relation between the radius of the silver(II), relatively larger compared with first series transition metal ions, and the space available for it within the isoindole group.<sup>15</sup>

16 Ag(II)TnPc has a typical MPc(-2) electronic spectrum (see Fig.6 below) in very dilute (ca  $10^{-5}$ M) solution.<sup>16</sup> More concentrated solutions (e.g.  $> 10^{-4}$ M) show additional absorption at 620nm indicative of aggregation common to phthalocyanine moieties.<sup>14,17-19</sup> Aggregation also occurs in very dilute solutions if they are cooled. Just above the freezing point of toluene ( $-95^{\circ}\text{C}$ ), the 620nm band, in a  $1.5 \times 10^{-5}$ M solution, has grown to some 83% of the intensity of the 678nm band, and the whole Q band region has broadened. As a result the ESR spectrum of the Ag(II) species, clearly observed at room temperature (see below) is lost rather than intensified at lower temperature.

17-19 Figs 1,2 Electrochemistry: Figs.1,2 show cyclic and differential pulse voltammograms for Ag(II)TnPc in DCB solution containing 0.2-0.4M TBAPF<sub>6</sub> as supporting electrolyte.

Ag(II)TnPc(-2): Oxidation processes: On the oxidation side positive of 0 volts vs SCE, there are three redox couples. The first, I(ox) is broad, diffuse and contains several closely spaced waves. The second, II(ox) is a well-behaved reversible process, with equal cathodic and anodic currents and a square root dependence upon scan rate. The third, III(ox), is irreversible, showing an oxidation component but no return cathodic component.

On the basis of spectroelectrochemistry (described below), the ill-defined

20 redox process I(ox) is assigned to the  $[\text{Ag(III)TNPc(-2)}]^+ / \text{Ag(II)TNPc(-2)}$  couple.<sup>20</sup> Controlled potential oxidation over this wave generates a stable solution of  $[\text{Ag(III)TNPc(-2)}]^+$  (coulometry confirms this is a one electron oxidation). The broad diffuse nature of couple I(ox) derives, at least in part, from aggregation phenomena in solution since the DPV peak becomes more narrow and better defined if the concentration is reduced. This is similar to the behaviour reported by Kadish and co-workers<sup>21</sup> for zinc octacyanophthalocyanine, where both the monomeric and aggregated forms of the species oxidize at similar but not identical potentials.

21 Forward and reverse DPV scans show significantly shifted broad waves suggestive of a shift in the equilibrium mixture of monomeric and aggregated AgTnPc depending upon whether one is approaching from Ag(II)TNPc(-2) or  $[\text{Ag(III)TnPc(-2)}]^+$  (Fig.1). One must conclude that the kinetics of this equilibrium are sluggish with respect to the voltammetry time scale even on the very slow time scale of DPV.

Using a nernstian plot of the spectroelectrochemical data over this first wave, yields a halfwave potential for the Ag(III)/Ag(II) process of 0.71V vs SCE. This is somewhat more positive than those for AgTPP and AgOEP, 0.54 and 0.44 respectively,<sup>4b</sup> showing, as anticipated, the greater thermodynamic stability of silver(II) in a phthalocyanine environment relative to a porphyrin environment.

The reversible process, II(ox), is  $[\text{Ag(III)TNPc(-1)}]^{2+} / [\text{Ag(III)TNPc(-2)}]^+$  with both the singly and doubly oxidized species being stable in DCB; it gives normal reversible forward and reverse DPV peaks, and is confirmed by coulometry to be a one electron oxidation.

The irreversible couple III(ox) is not so securely assigned and it is not stable enough for spectroelectrochemical elucidation. It appears to have more current associated with it than does the previous couple II(ox). It presumably involves the  $[\text{Ag(III)TNPc(0)}]^{3+} / [\text{Ag(III)TnPc(-1)}]^{2+}$  couple; possibly the  $[\text{Ag(III)TNPc(0)}]^{3+}$  generated is then oxidising solvent, or perhaps itself, resulting in some additional catalytic current.

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Ag(II)TNPc(-2): Reduction processes: In the electrochemistry of silver porphyrins, the Ag(II) central ion is reduced to Ag(I) prior to porphyrin ring reduction.<sup>4b,6</sup> However, demetallation is observed following the reduction of Ag(II) to Ag(I).<sup>22,23</sup> Well-defined CV waves for the Ag(II)TPP/[Ag(I)TPP]<sup>-</sup> reduction were observed with  $E_{1/2}$  at -1.01 V vs SCE in dichloromethane. In the same solvent, H<sub>2</sub>TPP is reduced at -1.21V vs SCE. The Ag(II)/Ag(I) reduction wave is rather broad and the current ratio  $I_{pa}/I_{pc}$  is less than unity at low sweep rates, and approaches unity at higher sweep rates. This is consistent with reduction of Ag(II)TPP to [Ag(I)TPP]<sup>-</sup> followed by demetallation at a rate comparable to the cyclic voltammetric time scale. Controlled potential electrolysis just negative of the Ag(II)/Ag(I) wave leads to the unmetallated free base. The lability of silver porphyrins was attributed to the fact that the diameter of Ag(I) ion is 1.26Å but that of Ag(II) is only 0.89Å.<sup>5</sup> Expulsion of Ag(I) from the porphyrin core evidently takes place.

Ag(II)TNPc has very similar electrochemical behavior. There are four reduction processes between 0 and -1.5V vs SCE, namely I(red), I'(red), II'(red) and II(red) (Fig.1), with I(red) and I'(red) overlapping, in the cyclic voltammogram. Wave II'(red) is a well-behaved reversible couple with equal cathodic and anodic currents and a square root dependence upon scan rate. Controlled potential reduction just negative of the first composite wave (I(red)) leads only to the reduced metal free [H<sub>2</sub>TNPc(-3)]<sup>-</sup> anion radical.

The composite nature of this first reduction is more clearly demonstrated in the DPV voltammogram which shows two peaks separated by ca 95mV. In the CV experiment, with increasing scan rate, peak I(red) shifts more negatively, moving underneath peak I'(red) which only shifts slightly negative under these conditions (Fig.2). Couple II(red) becomes more obvious at higher scan rates, with intensity growing at the expense of couple II'(red). It is largely absent from the very slow scans, especially for example the DPV scans which are carried out at 2 mV/s. Normal forward (negative going from 0 V) and reverse (positive going from negative poten-

tials towards 0 V) DPV scans are observed for couples I'(red) and II'(red), but I(red) appears only in the forward DPV scan (Fig.1). In the cooled solution, (Fig.3A), wave I(red) becomes highly irreversible, while wave II'(red) becomes relatively less intense and wave II(red) becomes relatively more intense.

These data lead to the following redox assignments (Table 1):-

I(red)  $\text{Ag(II)TNPc}(-2)/[\text{Ag(I)TNPc}(-2)]^-$   $E_{irr}$

followed by:-

$[\text{Ag(I)TNPc}(-2)]^- + 2\text{H}^+ \longrightarrow \text{H}_2\text{TNPc}(-2) + \text{Ag(I)} \quad C_{irr} \text{ (slow)}$

followed by:-

I'(red)  $\text{H}_2\text{TNPc}(-2)/[\text{H}_2\text{TNPc}(-3)]^-$   $E_{rev}$

II'(red)  $[\text{H}_2\text{TNPc}(-3)]^-/[\text{H}_2\text{TNPc}(-4)]^{2-}$   $E_{rev}$

and

II(red)  $[\text{Ag(I)TNPc}(-2)]^-/[\text{Ag(I)TNPc}(-3)]^-$   $E_{rev}$

The voltammetry of  $\text{H}_2\text{TNPc}$  (described briefly below) shows two reduction processes at the same potentials as I'(red) and II'(red), and indeed addition of some  $\text{H}_2\text{TNPc}$  to a  $\text{Ag(II)TNPc}$  solution results in a comparative increase in the currents for I'(red) and II'(red). Further the voltammogram for  $\text{H}_2\text{TNPc}$  does not show a wave in the position for II(red) confirming that it is a silver based couple.

The demetallation of  $[\text{Ag(I)Pc}]^-$  likely proceeds through a hydrolysis step involving trace moisture in the solvent. However intensive drying of the solvent with molecular sieves did not materially alter the electrochemistry described here. At high scan speeds, there is less time for demetallation of  $\text{Ag(I)TNPc}(-2)$  and therefore II'(red) is suppressed and the second silver phthalocyanine reduction, II(red) is enhanced. Similarly at low temperatures, demetallation is suppressed.

Redox process I(red) shifts to more negative potentials with increasing scan rate because it is an  $E_{irr}C_{irr}$  process; because of the overlapping nature of the band, detailed analysis of this shift with scan rate is deferred. The electron

F<sub>15</sub> transfer irreversibility is indicated by the fact that even at low temperatures little or no return current can be assigned to I(red) (Fig.3A). This is also clearly seen in Fig.3B which shows the behaviour in dichloroethane.

The absence of a reverse DPV peak for I(red) is a consequence of the build-up of H<sub>2</sub>TNPc and a depletion of AgTNPc in the vicinity of the electrode when scanned from very negative potentials.

24 More detailed consideration of the relative currents evident in the low temperature voltammogram (Fig.3A) suggests that there may be an intermediate step between the reduction of Ag(II)TNPc and the hydrolysis of [Ag(I)TNPc]<sup>-</sup> since less metal free H<sub>2</sub>TNPc appears present than a rough estimate of the amount of AgTNPc which has hydrolysed.<sup>24</sup> One might have also expected that the Ag(II)/Ag(I) electron transfer step would have shown reversibility at low temperature when the hydrolysis was partially suppressed since metal couples within MPc units are usually reversible in the absence of a following reaction. Possibly the intermediate causing irreversibility is a sitting-atop Ag(I)TNPc species, the large metal ion having popped out of the plane of the macrocycle.

There are some alternative assignments for the redox electrochemistry which must be considered but which may in fact be rejected:-

I(red)

II(red)

- i)  $\text{Ag(II)TNPc}(-2)/[\text{Ag(II)TNPc}(-3)]^-$   $[\text{Ag(II)TNPc}(-3)]^-/[\text{Ag(II)TNPc}(-4)]^{2-}$
- ii)  $\text{Ag(II)TNPc}(-2)/[\text{Ag(II)TNPc}(-3)]^-$   $[\text{Ag(II)TNPc}(-3)]^-/[\text{Ag(I)TNPc}(-3)]^{2-}$

The couples in assignment (i), by analogy with the copper TNPc species<sup>12</sup> and species such as H<sub>2</sub>TNPc reported here, would be separated by about 0.3 - 0.4V, and not, as observed here, ca 0.65V. Assignment (ii) is also logically unacceptable for the same reason, i.e.  $[\text{Ag(II)TNPc}(-3)]^-$  would be reduced to  $[\text{Ag(II)TNPc}(-4)]^{2-}$ , some 0.3-0.4V negative of I(red), before reduction to  $[\text{Ag(I)TNPc}(-3)]^{2-}$  could take place.

The assignments chosen here (Table 1) are also supported by the observation that the reduction process  $[\text{Co(I)TNPc}(-2)]^- / [\text{Co(I)TNPc}(-3)]^{2-}$  occurs, in DCB, at a potential very close to that of process II(red).<sup>12</sup>

#### H<sub>2</sub>TNPc(-2):

*F<sub>10</sub> 4* The voltammogram for this species in DCB is shown in Fig. 4, with data collected in Table 1. This species was explored briefly to obtain data with which to compare the AgTNPc behaviour described above. There are two clearly defined reversible reduction processes, I'(red) and II'(red), uniquely assignable to  $\text{H}_2\text{TNPc}(-2) / [\text{H}_2\text{TNPc}(-3)]^-$  and  $[\text{H}_2\text{TNPc}(-3)]^- / [\text{H}_2\text{TNPc}(-4)]^{2-}$  respectively.

Positive of zero volts are seen two redox processes curiously similar to the AgTNPc data described here. There is a broad redox wave positive of zero, I'(ox), which must arise from oxidation of both mononuclear and aggregated  $\text{H}_2\text{TNPc}(-2)$  to  $[\text{H}_2\text{TNPc}(-1)]^+$ . The more positive and reversible redox process, II'(ox) is then assigned to  $[\text{H}_2\text{TNPc}(0)]^{2+} / [\text{H}_2\text{TNPc}(-1)]^+$ .

#### Spectroelectrochemistry of AgTNPc Species

*F<sub>10</sub> 5* Stepwise controlled potential oxidation from 0.55V to 0.9V (vs. SCE) of a solution of Ag(II)TNPc in DCB with TBAPF<sub>6</sub> as supporting electrolyte results in the spectroscopic changes shown in Figure 5a, and a change in solution colour from blue to greenish-yellow. Isosbestic points are observed at 395, 557 and 703 nm. The final spectrum is consistent with that of a MPc(-2) species, and not of an oxidized MPc(-1) species,<sup>14,20</sup> and therefore oxidation to  $[\text{Ag(III)TNPc}(-2)]^+$  has occurred. Both Q-band and Soret band shift to longer wavelength by about 40 nm in the Ag(III) species compared with the Ag(II) species.

Figure 5b shows the spectrum development in the stepwise controlled potential electrolysis at the range of 1.10V to 1.40V, of the  $[\text{Ag(III)TNPc}(-2)]^+$  generated by bulk electrolysis at 0.95V. Isosbestic points are found at 612 and 752 nm. The solution colour changes from greenish yellow to dark grey. During this oxidation, the Q-band loses intensity and broad low-intensity bands appear in the 500-600nm



25 and 800-900nm regions. These are characteristic of the formation of radical  $\text{Pc}(-1)$  species<sup>13,14,17,20,25</sup>, specifically  $[\text{Ag}(\text{III})\text{TNPc}(-1)]^{2+}$ .

The spectroscopic changes for both oxidation steps (Figs. 5a and 5b) were reversible, and the original  $[\text{Ag}(\text{III})\text{TNPc}]^+$  and  $\text{Ag}(\text{II})\text{TNPc}$  spectra were generated by reverse stepwise controlled potential reductions from 1.35 to 1.10V and from 0.9 to 0.5V, respectively. Thus these data confirm the electrochemical assignments indicated above (Table 1).

Plots of  $\log[(A_0 - A)/(A - A_p)]$  vs. potential for the two oxidation steps and their re-reductions gave the expected linear plots. Zero intercepts give an apparent  $E_{1/2}$  of 0.71V for the  $[\text{Ag}(\text{III})\text{TNPc}(-2)]^+/\text{Ag}(\text{II})\text{TNPc}(-2)$  couple (data from Fig. 5a at 685nm) and 1.25V for the  $[\text{Ag}(\text{III})\text{TNPc}(-1)]^{2+}/[\text{Ag}(\text{III})\text{TNPc}(-2)]^+$  couple (data from Fig. 5b at 722nm). The latter line has a slope of 77mV (average of forward and reverse experiments) close to the anticipated 59mV for a one-electron redox process. The former line has an average slope of about 110mV, larger than expected; the reason for this is not apparent. The spectroelectrochemical data were obtained at a concentration some 10-20 times more dilute than the electrochemical data, in a regime where aggregation though present is very much less important.

F<sub>6</sub> Figure 6 shows the electronic absorption spectra of  $\text{Ag}(\text{II})\text{TNPc}$  and the electrochemically generated  $[\text{Ag}(\text{III})\text{TNPc}(-2)]^+$  and  $[\text{Ag}(\text{III})\text{TNPc}(-1)]^{2+}$  species. Absorption maxima and molar absorptivity data are given in Table 2.

26,27 Electron spin resonance The  $\text{Ag}(\text{II})$  species has a  $d^9$  configuration with one unpaired electron. Extensive ESR studies have been carried out on silver(II) N-heterocyclic complexes<sup>2</sup> and silver(II) porphyrins<sup>26,27</sup>, and also the isoelectronic copper(II) phthalocyanines<sup>28</sup>. Few ESR data are available for silver phthalocyanines. MacCragh and Koski<sup>15</sup> reported some ESR parameters for  $\text{AgPc}$  in 1963 within work mainly devoted to porphyrin species. They experienced difficulties because of the low solubility and lability of the species.

The ESR spectra of  $\text{Ag}(\text{II})\text{TNPc}$  in chloroform at room temperature and diluted

with H<sub>2</sub>TNPc, in chloroform/toluene glass at 98K are shown in Figures 7a and 7b. Dilution with H<sub>2</sub>TNPc is necessary to reduce the effects of relaxation caused by aggregation when solutions of Ag(II)TNPc are cooled. Evidently H<sub>2</sub>TNPc can replace Ag(II)TNPc in aggregated species yielding Ag(II)TNPc.H<sub>2</sub>TNPc aggregates which generate fine quality ESR spectra.

Silver has two isotopes, both of nuclear spin of 0.5, and of approximately equal abundance. There are four equivalent nitrogen atoms each with nuclear spin 1.0. Thus, assuming equal coupling to the two silver isotopes, there could be 18 lines in the spectra of each of the parallel and perpendicular orientations. The isotropic spectrum shows 11 roughly equally spaced lines (Fig.7a) which arise if the silver isotropic hyperfine coupling constant is (approximately) twice that of the nitrogen isotropic hyperfine coupling constant. The frozen solute ESR spectrum (Fig.7b) is resolved into at least 24 lines. Following the analysis used by Koski et al<sup>15,26</sup> in their studies on copper and silver porphyrins, computer simulation of the anisotropic spectrum yielded the spin Hamiltonian parameters given in Table 3. Though the quality of the data reported here exceeds that of data published previously<sup>15</sup>, the actual parameters derived here for Ag(II)TNPc/H<sub>2</sub>TNPc, in DCB, do not differ significantly from those of Ag(II)Pc in 1-chloronaphthalene.

Conclusion: Silver(II) tetraneopentoxypthalocyanine is a well characterized silver phthalocyanine whose solubility in organic solvents should make it valuable for future film studies. It is especially pertinent that both the one and two electron oxidation products are also stable. Future studies will explore this oxidation chemistry in film phase.

Acknowledgements: We are indebted to the Natural Sciences and Engineering Research Council (Ottawa) and the Office of Naval Research (Washington) for financial assistance.

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### Figure Legends

Figure 1. Cyclic and differential-pulse voltammograms Ag(II)TNPc in DCB solution containing ca. 0.2 M TBAPF<sub>6</sub>. Scan rates: 100mV/s for CV and 2mV/s for DPV. In the electrochemical studies, the concentration of AgTNPc is ca.  $5 \times 10^{-4}$  -  $1 \times 10^{-3}$  M.

Figure 2. Variable scan rate cyclic voltammograms for Ag(II)TNPc in DCB/TBAPF<sub>6</sub> (reduction processes). Scan rates (inner to outer):- 20, 50, 100, 200 and 500 mV/s.

Figure 3. A. Cyclic voltammogram for reduction of Ag(II)TNPc at -15°C in DCB/TBA PF<sub>6</sub>. Scan rate 100 mV/s. B. Cyclic voltammogram for reduction of Ag(II)TNPc at room temperature in DCE/TBA PF<sub>6</sub>. Scan rate 100 mV/s.

Figure 4. Cyclic voltammogram of H<sub>2</sub>TNPc in DCB/TBAPF<sub>6</sub>. Scan rate 100mV/s.

Figure 5. Stepwise controlled spectroelectrochemistry. (a) Ag(II)TNPc in DCB solution showing the development of [Ag(III)Pc(-2)]<sup>+</sup> as potential is stepped through the first oxidation wave from 0.55 to 0.9V vs SCE; (b). Electrochemically generated [Ag(III)Pc(-2)]<sup>+</sup> in DCB showing the development of the  $\pi$ -cation radical [Ag(III)Pc(-1)]<sup>2+</sup> as the potential is stepped through the second oxidation wave from 1.10 to 1.40V vs SCE. The solutions contain ca 0.2M TBA PF<sub>6</sub>. The absorbance value for the main peak near 722 nm, ca. 2.00, is rather high, and the top of the band may be clipped slightly. The data in Fig.6 are more accurate. Base line "glitches" near 803 and 941 nm are machine artifacts and should be ignored. The concentration of Ag(II)TNPc is ca  $3 \times 10^{-5}$  M.

Figure 6. Electronic absorption spectra. (A) (----) Ag(II)TNPc in DCB: (B) (....) electrochemically generated [Ag(III)TNPc(-2)]<sup>+</sup> and (C) (----) [Ag(III)TNPc(-1)]<sup>2+</sup> in DCB solution with ca 0.2M TBAPF<sub>6</sub>. Note that the first two spectra are plotted versus the left-hand y axis, while the third spectrum is expanded through use of the right-hand y axis. Base line "glitches" near 373, 803, and 941 nm are machine artifacts and should be ignored.

Figure 7. Electron spin resonance spectra of Ag(II)TNPc. (a). in chloroform solution at room temperature. (b). in a mixed chloroform/toluene (1:1, v:v) solvent, at

5/31/90 AgTnPc.pap --16--

98K, containing ca  $10^{-3}\text{M}$   $\text{H}_2\text{TNPc}$  to reduce the self-aggregation of the silver species.

Table 1. Electrochemical Data in Dichlorobenzene Solution<sup>a</sup>

$E_{1/2}, V(\Delta E_p, mV)$		Assignments
Ag(II)TNPc	H <sub>2</sub> TNPc	
Oxidation:		
III(ox)	1.72irr	$[Ag(III)Pc(0)]^{3+} / [Ag(III)Pc(-1)]^{2+}$
II'(ox)	1.38(120)	$[H_2TNPc(0)]^{2+} / [H_2TNPc(-1)]^{+}$
II(ox)	1.19(80)	$[Ag(III)Pc(-1)]^{2+} / [Ag(III)Pc(-2)]^{+}$
II'(ox)	0.9irr	$[H_2TNPc(-1)]^{+} / H_2TNPc(-2)$
I(ox)	0.71irr	$[Ag(III)Pc(-2)]^{+} / Ag(II)Pc(-2)$
Reduction:		
I(red)	-0.79 <sup>b</sup>	$Ag(II)TNPc(-2) / [Ag(I)TNPc(-2)]^{-}$
I'(red)	-0.90(70)	$H_2TNPc(-2) / [H_2TNPc(-3)]^{-}$
II'(red)	-1.20(130)	$[H_2TNPc(-3)]^{-} / [H_2TNPc(-4)]^{2-}$
II(red)	-1.47(100) <sup>c</sup>	$[Ag(I)TNPc(-2)]^{-} / [Ag(I)TNPc(-3)]^2$

a) Potentials are reported with respect to SCE.  $E_{1/2}$  values measured by cyclic voltammetry at 20 mVs<sup>-1</sup> [ $E_{1/2} = (E_{pa} + E_{pc})/2$ ]. Peak to peak potentials reported in parenthesis. irr = irreversible. b) Cathodic peak potential from differential-pulse voltammetry at 2mV/s. c) Peak to peak potential at 200mV/s scan rate.

Table 2. Electronic Absorption Maxima<sup>a</sup>

LAMBDA  
OR  
EPSILON

Species	$\lambda_{\text{MAX}}, \text{nm}$ ( $\epsilon/10^4, \text{M}^{-1}\text{cm}^{-1}$ )				
Ag(II)TNPc(-2)	356 (1.33)	386 (1.07)	618 (2.12)	685 (7.61)	
[Ag(III)TNPc(-2)] <sup>+b</sup>	361 (0.80)	424 (1.77)	647 (2.02)	722 (6.78)	
[Ag(III)TNPc(-1)] <sup>2+b</sup>		439 (1.92)	574 (1.14)	649 (0.95)	721 (1.06)
					854

a. DCB solution. b. Solutions contain about 0.2M TBAPF<sub>6</sub>.

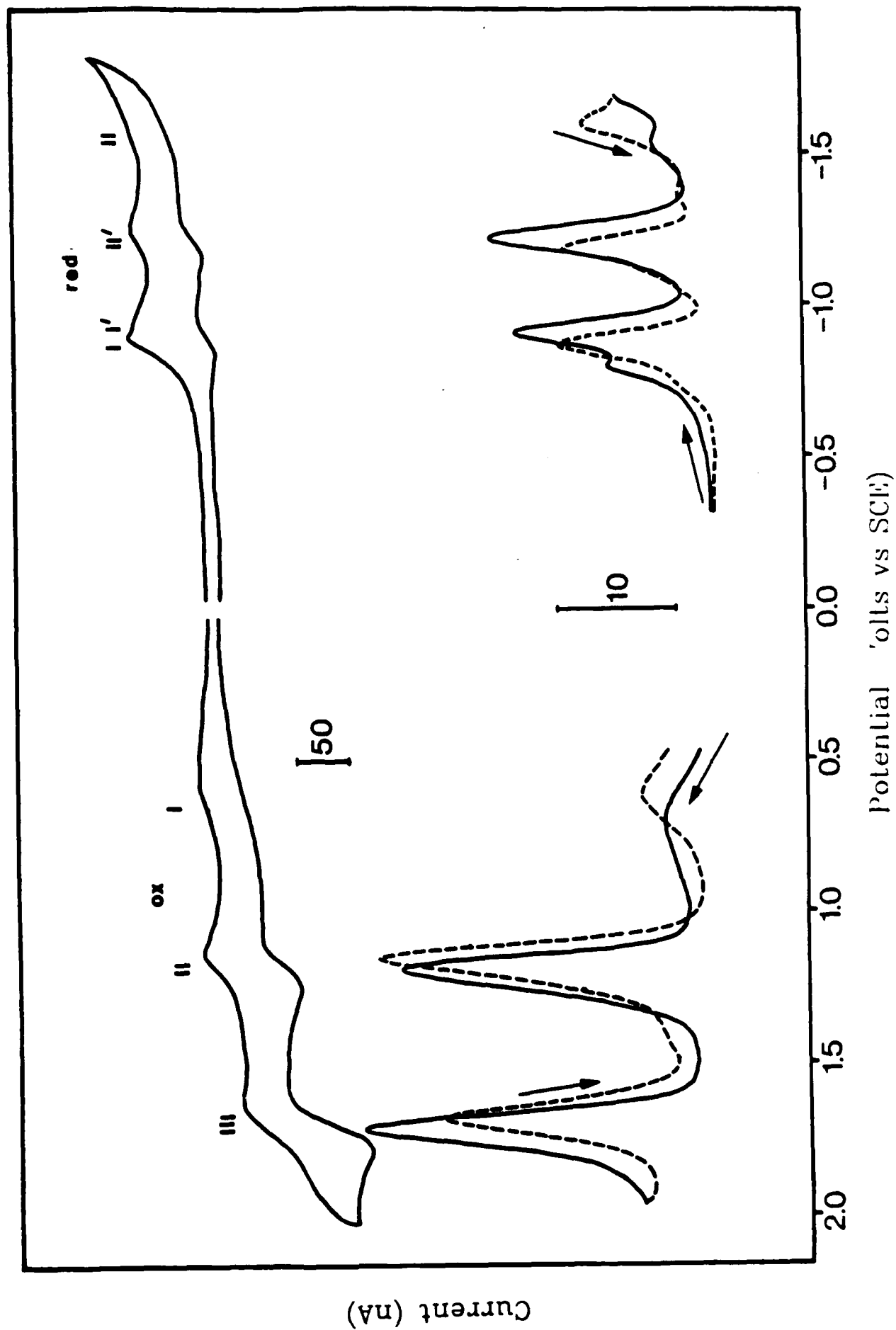


Table 3. Spin Hamiltonian Parameters

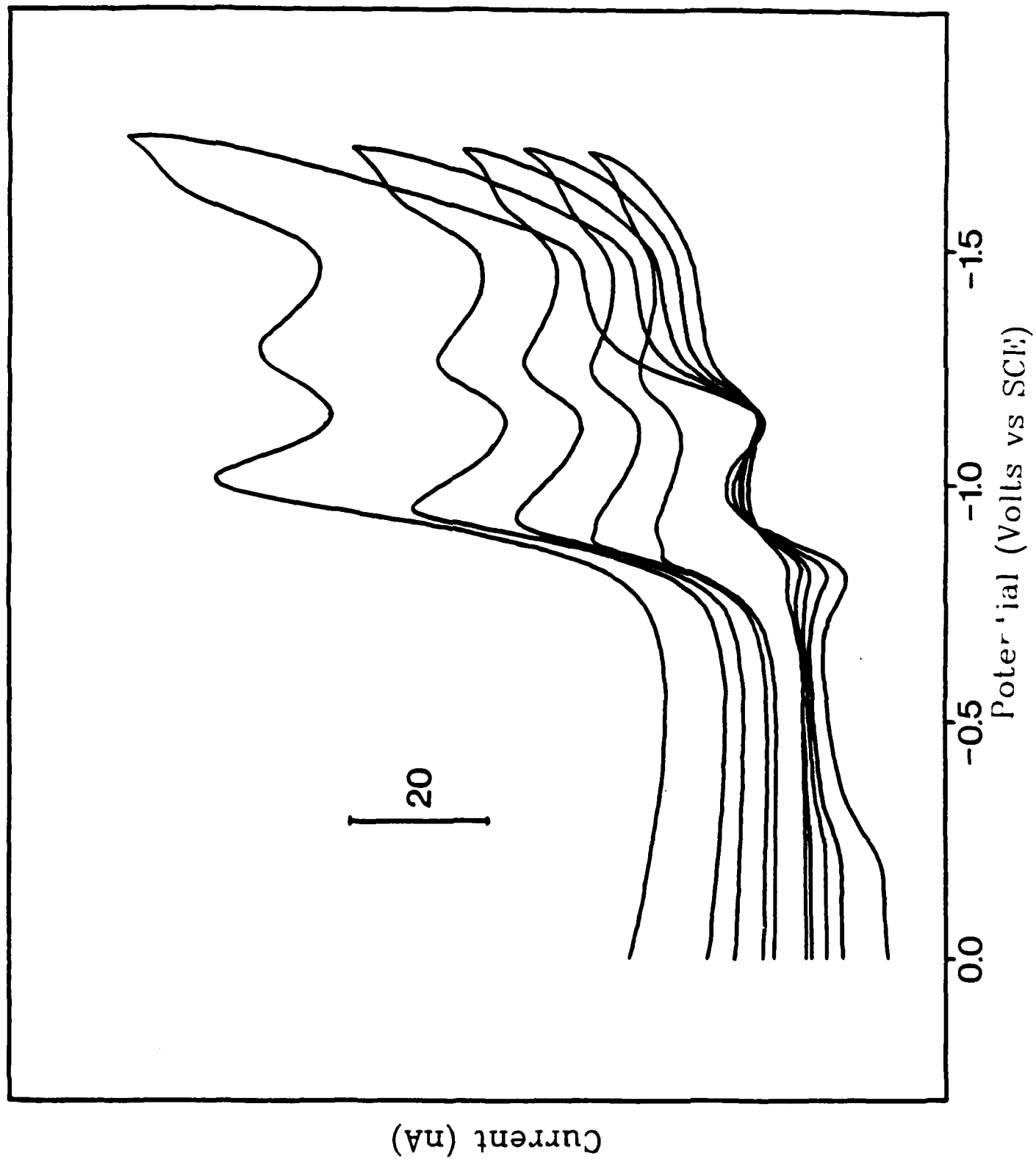
$g$ Value		Hyperfine Coupling to Silver.		Superhyperfine to Nitrogen.	
			Gauss		Gauss
$g_{iso}$	2.049	a	52	b	23.6
$g_{  }$	2.087	A	40	C	20
$g_{\perp}$	2.030	B	58	D	25.4

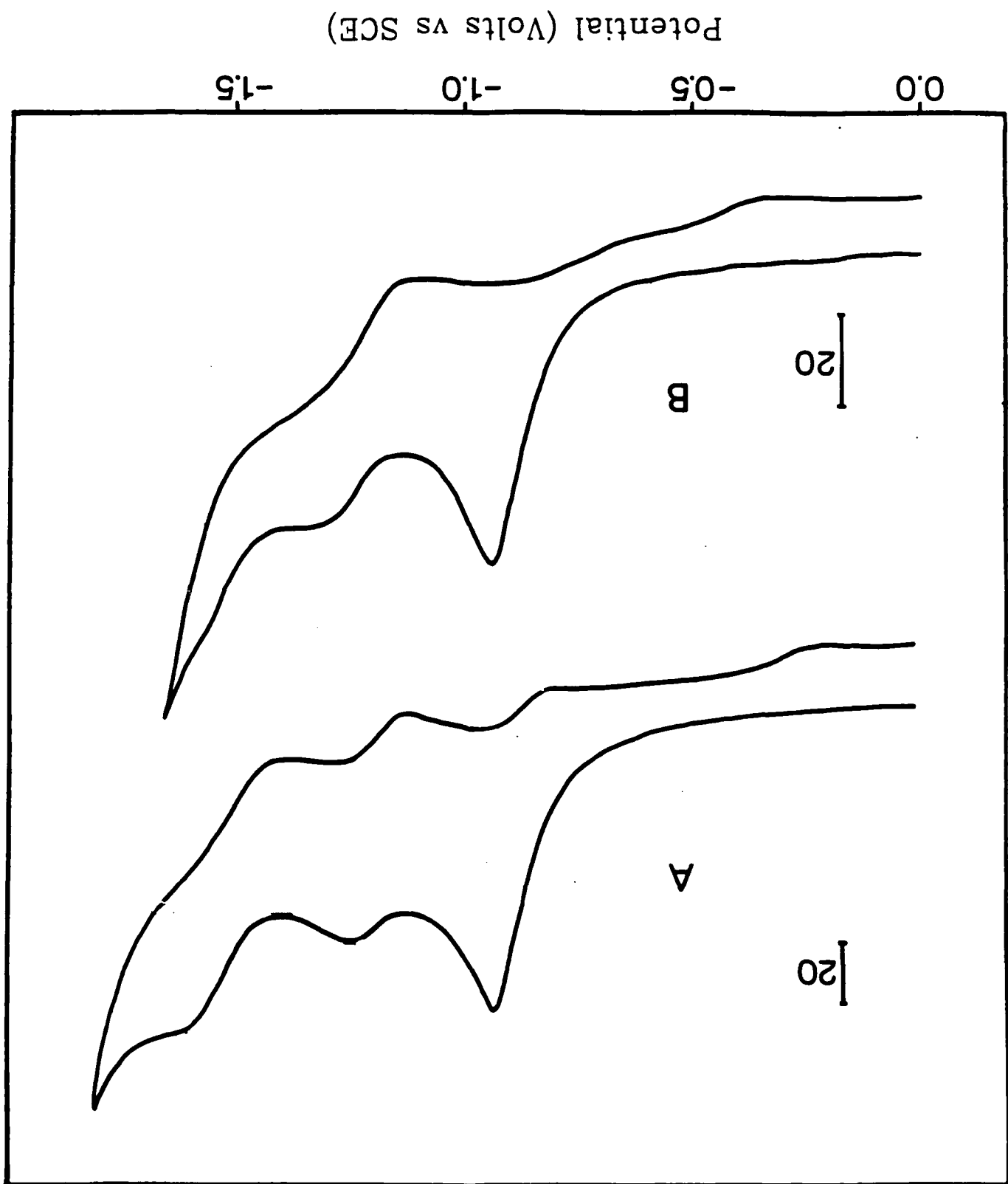
Footnotes: a,b are the isotropic hyperfine coupling constants to silver and nitrogen respectively. A,B are the anisotropic hyperfine coupling constants, parallel and perpendicular to silver respectively. C,D are the anisotropic hyperfine coupling constants, parallel and perpendicular to nitrogen respectively.

F.1

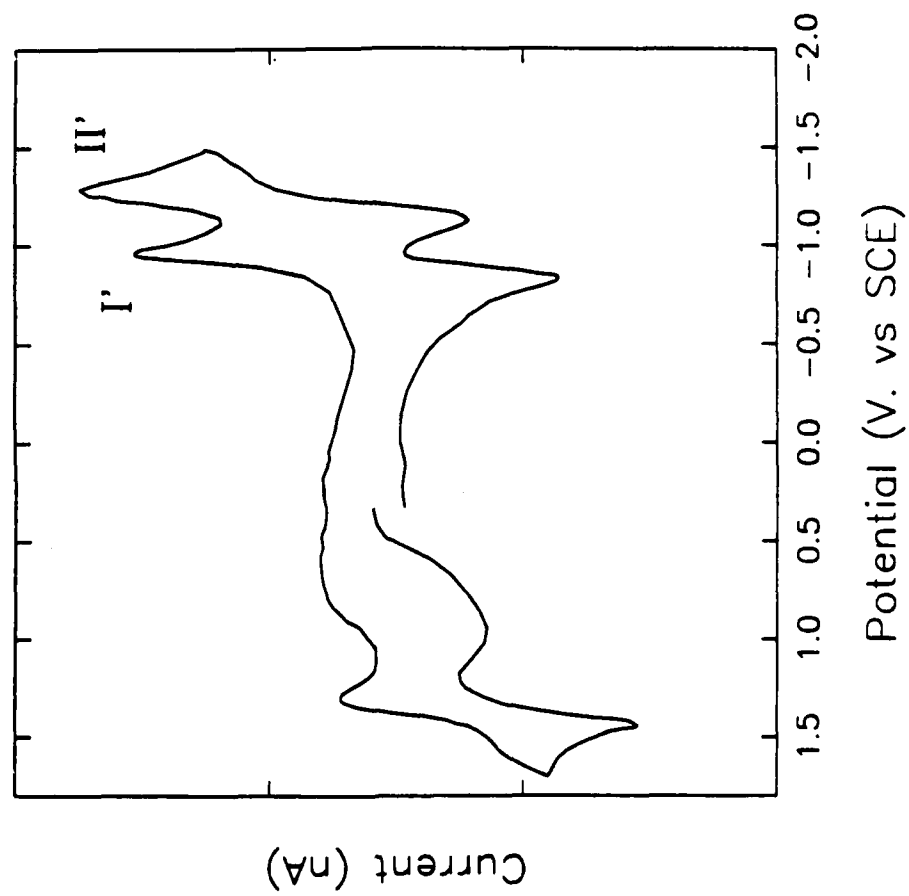


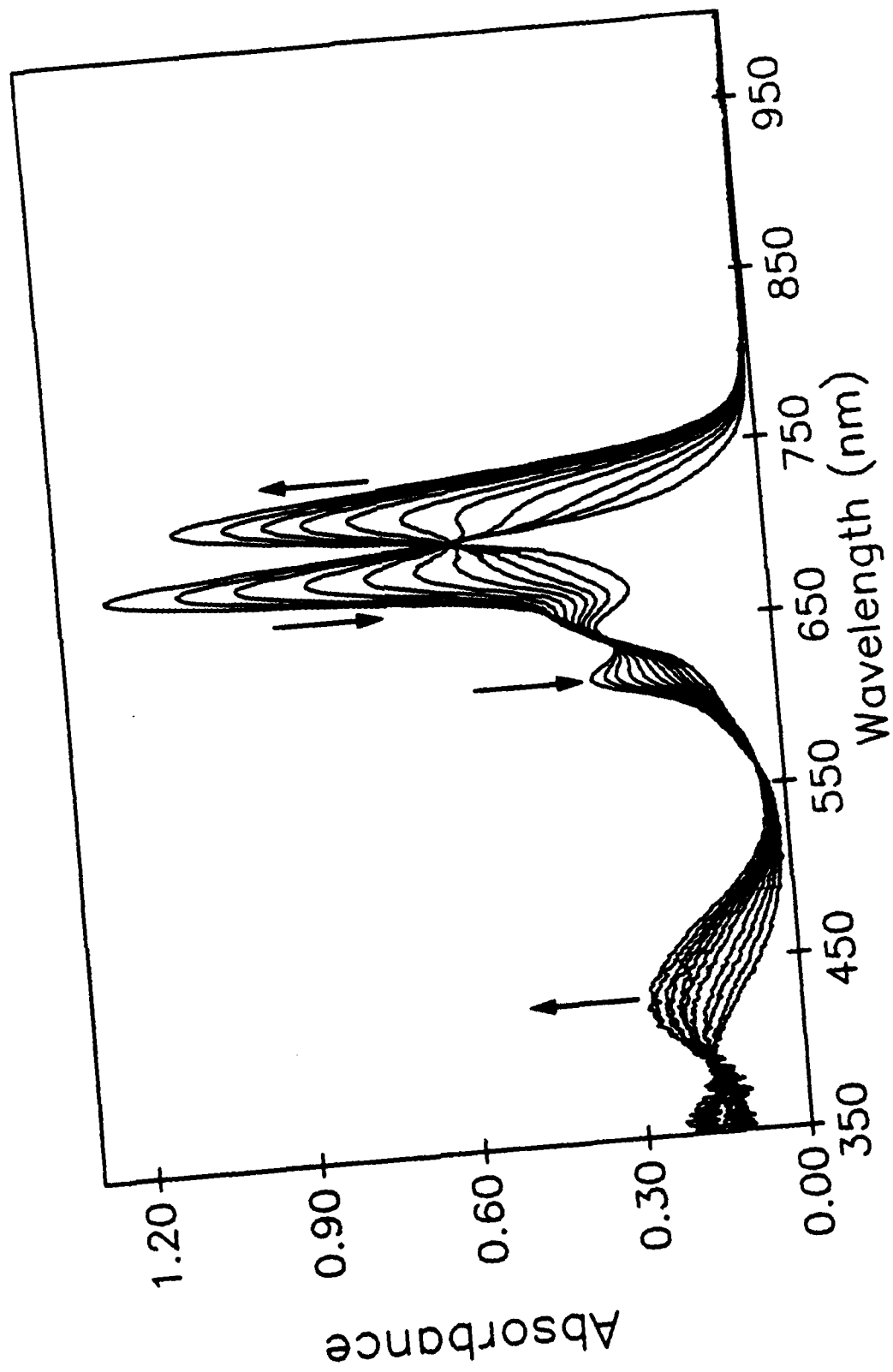
F. 2

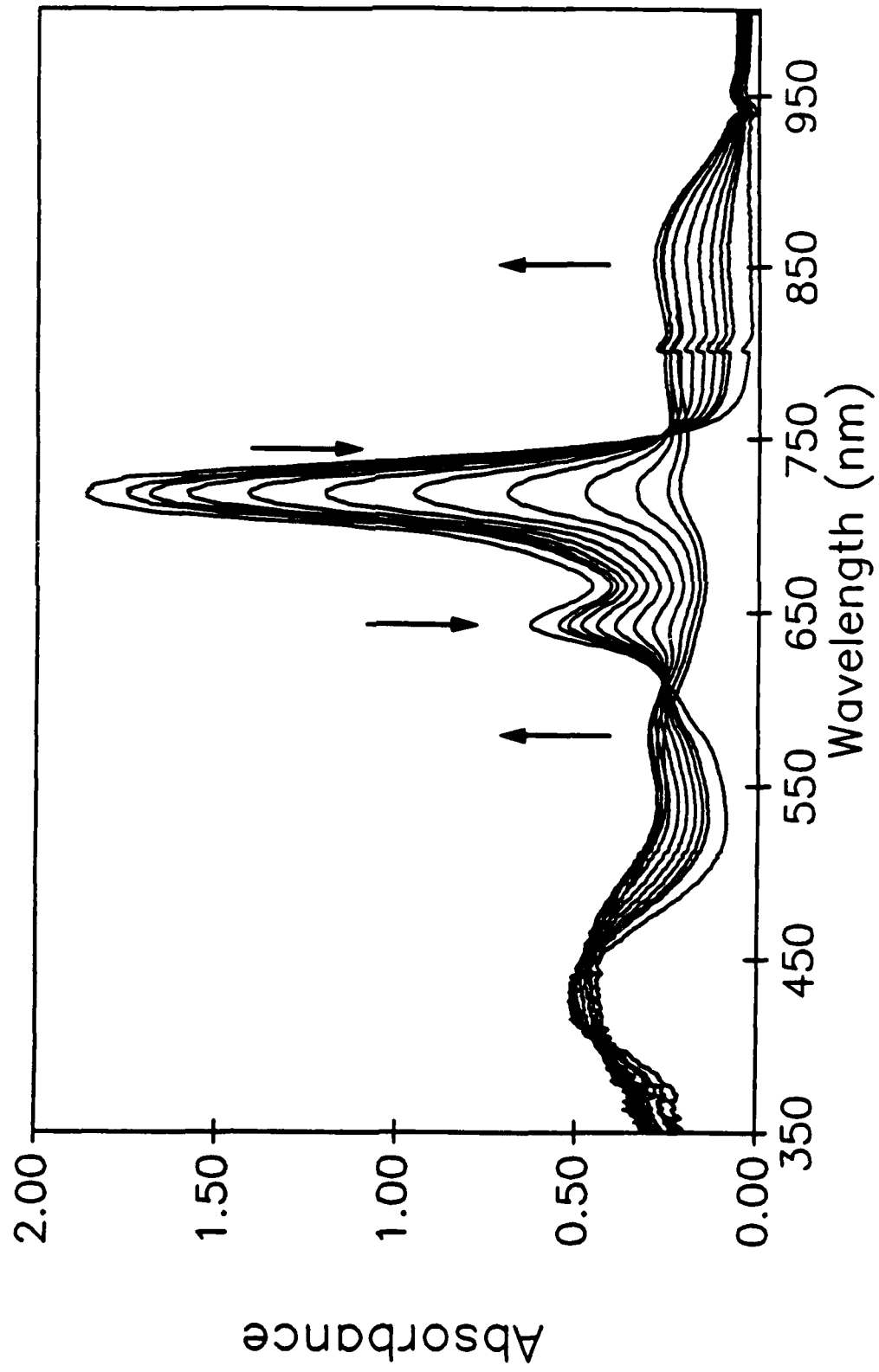




4

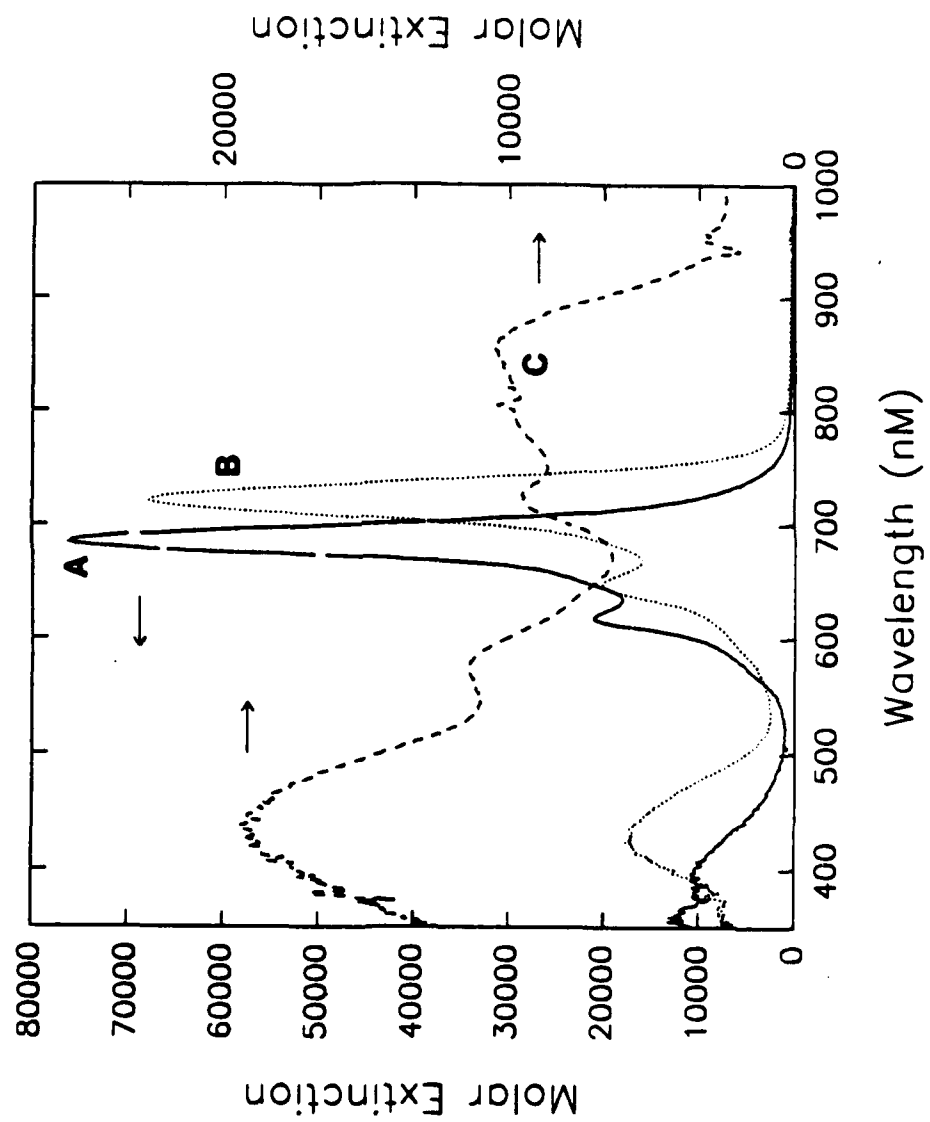






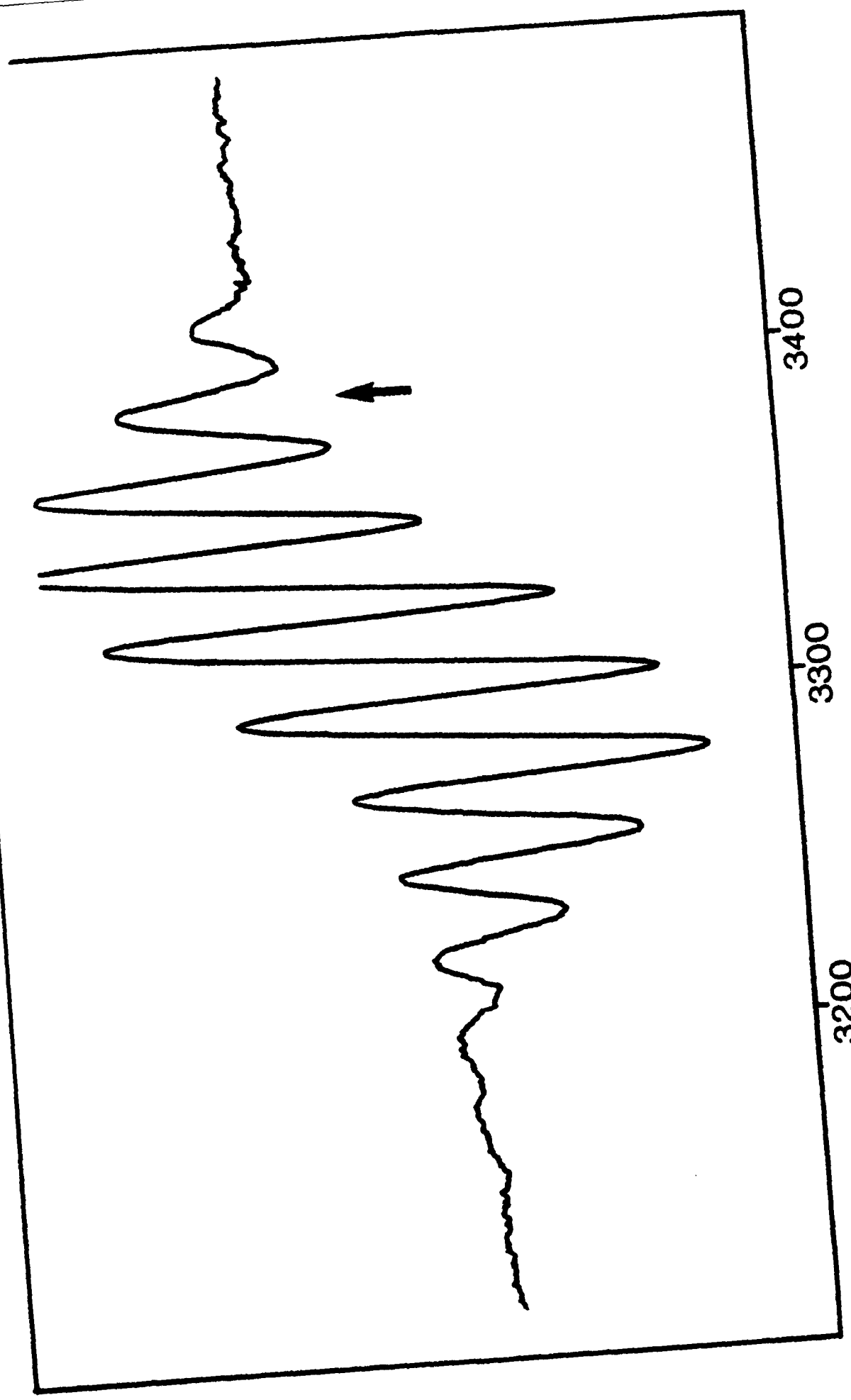
F<sub>13</sub>6

F<sub>15</sub>6





F3 7 A



3400

3300

3200

Gauss

137.6

